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# ABSTRACT

The diffusion of radioactive sulfur ( $S^{35}$ ) into single crystals of lead sulfide has been studied as a function of deviation from stoichiometry and defect concentration introduced by doping, in the temperature range  $773^{\circ}\text{K}$  to  $1023^{\circ}\text{K}$ , in order to determine the predominant mechanism by which the anion diffuses in this compound. Measurements have been made using crystals whose composition varied from  $3 \times 10^{18}$  excess sulfur atoms per cc. to  $5 \times 10^{18}$  excess lead atoms per cc. The sulfur excess specimens showed the highest diffusivities in this temperature range, whereas lowest diffusion coefficients were obtained in the lead excess specimens. Diffusion measurements have also been performed on specimens doped with 0.5 or 0.05 mole percent  $\text{Ag}_2\text{S}$  or  $\text{Bi}_2\text{S}_3$ , which were annealed under the same conditions as those required to obtain undoped stoichiometric  $\text{PbS}$  crystals.

Results indicate that the nature of the bonding forces between the components of  $\text{PbS}$  may be the most important single factor in determining the process by which diffusion occurs in partially polar compounds. The data is consistent with jumps of divalent, negatively charged sulfur ions into anion vacancies as a mode of diffusion only in  $\text{PbS}$  containing a large excess of lead. In lead sulfide containing excess of sulfur, or small excess lead concentrations, sulfur is believed to diffuse primarily as a small, positively charged species, by jumps into vacancies in the cation sublattice, or by some interstitial mechanism.

# SELF DIFFUSION OF SULFUR-35 IN SINGLE CRYSTALS OF LEAD SULFIDE

## INTRODUCTION

In recent years it has become apparent that point defects, such as interstitial atoms, vacancies, and foreign ions may greatly influence the properties of crystalline materials. The small deviations from the stoichiometric composition which occur in the partially polar compounds PbS, PbSe and PbTe offers a method for controlling the concentration of point defects present in these materials and so allows for a study of physical properties such as diffusion and conductivity as a function of defect concentration. The properties of these compound semiconductors may also be influenced by the addition of foreign elements which enter the crystal under the formation of vacancies or interstitials in the lattice. Over the limited range of composition where the laws of mass action holds, the situations which obtain upon the addition of monovalent and trivalent cations to PbS have been described by C. Wagner<sup>1</sup> and J. Bloem<sup>2</sup>.

In a previous report<sup>3</sup>, we have presented the results of an investigation of the self diffusion in inert atmospheres, of Pb<sup>210</sup> into lead selenide single crystals, undoped and with monovalent or trivalent cation additives. It was concluded that Frenkel defects of the cation type predominate in PbSe, and that diffusion of lead in this compound occurs predominantly by an interstitial mechanism.

The work of Simkovich and Wagner<sup>4</sup> on self diffusion of Pb<sup>210</sup> in lead sulfide single crystals indicates that cationic Frenkel disorder is the primary defect species for undoped PbS. In that work, specimens were heated in various sulfur atmospheres which allowed for control of defect concentration through variation of specimen composition, as well as by the doping technique used in the PbSe study.

In the present report we present the results of a study of diffusion of the anion species,  $S^{35}$  in lead sulfide single crystals, as a function of stoichiometry and defect concentration introduced by doping. This investigation was carried out in order to obtain a better understanding of the defect structure of PbS. The information may also be useful in comparing activation energies for diffusion with that of steady-state creep, limited by self diffusion<sup>5</sup>. The availability of self diffusion data for  $Pb^{210}$  and  $S^{35}$  in PbS may permit a verification of the theory of interdiffusion in binary ionic semiconductors as proposed by R.F. Brebrick<sup>6</sup>.

### THEORY

In self diffusion studies on the classical ionic compounds such as the alkali halides, contributions from conduction electrons and holes to the electrical neutrality condition are not considered, since the electronic conductivity is small. Lead sulfide however has a small energy gap and electrical conduction takes place in this material primarily by the movement of quasi free electrons or holes. A determination of the number of point defects present at thermodynamic equilibrium in PbS must therefore include electronic defects in the electro-neutrality and mass action law relationships governing the equilibrium between the defects. Assuming the most general condition in which both lead and sulfur vacancies and interstitials can exist in equilibrium along with the electronic defects, the following relations are obtained from the law of mass action:

- (1)  $K_i = np = n_o^2 \exp(-E_i/kt)$
- (2)  $K_s = [V_{Pb}'] [V_S'] = K_s^o \exp(-E_s/kt)$
- (3)  $K_F(Pb) = [Pb_i'] [V_{Pb}'] = K_F(Pb)^o \exp(-E_F(Pb)/kt)$
- (4)  $K_F(S) = [V_S'] [S_i'] = K_F(S)^o \exp(-E_F(S)/kt)$
- (5)  $K_I = [S_i'] [Pb_i'] = K_I^o \exp(-E_i/kt)$

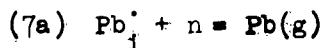
where  $n$  is the concentration of conduction electrons,  $p$  is the concentration of holes,  $[V_{Pb}']$  is the concentration of cation vacancies,  $[V_S']$  is concentration of anion vacancies,  $[S_i']$  is the concentration of anion interstitials,  $[Pb_i']$  is the concentration of lead interstitials,  $K_1$ ,  $K_s$  etc. are the equilibrium constants for the various defect pairs shown in Eqs. 1-5, and  $E_1$ ,  $E_s$ , etc. are the energies required to form the defect pairs. In Eqs. 1-5 the notation of Kröger and Vink<sup>7</sup> has been used, where the superscript heavy dots represent positive charge remaining on the center and primes mean negative charge remaining on the center. From experiments on electron conduction as a function of sulfur pressure, Bloem<sup>2</sup> has shown that defects in lead sulfide exist primarily in the singly ionized state, thus Eqs. 1-5 are written as indicated.

If the PbS lattice is assumed to be formed predominantly from divalent lead and sulfur atoms, then the electro-neutrality condition, which states that the crystal as a whole is neutral, may be written as follows:

$$(6) \quad [V_S'] + p + [Pb_i'] = [V_{Pb}'] + n + [S_i']$$

This relation may be simplified by the fact that certain of the above defects may dominate the others at equilibrium under a given sulfur pressure. Relation 6 is independent of the type of bonding which predominates in PbS.

It is also possible to establish relationships between the partial pressure of one of the components of PbS and the defect species present in the compound. For example, the reaction in which lead enters the PbS lattice interstitially from the gas phase may be formulated as follows:



It follows that:

$$(7b) \quad [Pb_i'] n = K_1 p_{Pb}$$

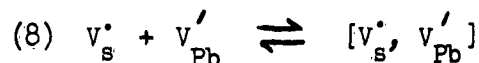
where  $K_1$  is an equilibrium constant and  $p_{Pb}$  is the partial pressure of lead.

Kröger and Vink<sup>7</sup> indicate how one can obtain diagrams in which concentrations of the various defects which exist in a given system at a particular temperature may be plotted linearly as a function of the partial pressure of one of the components. This is accomplished by taking the logarithms of both sides of equations of the type given by Eqs. 1-7 in this paper. As a result of the fact that different defects predominate in the electroneutrality condition at different partial pressures there are ranges in these concentration-pressure diagrams in which the various defects have a given pressure dependence. One such diagram<sup>8</sup> for undoped PbS is shown schematically in Fig. 1 and will be discussed in more detail elsewhere in this report. It should be pointed out that the defect concentrations represented by the lines in Fig. 1 are those which exist at the temperature for which the diagram is drawn. While the atomic defects may be frozen in on quenching, one can expect a variation in electron and hole concentrations upon cooling specimens from elevated temperatures.

Diagrams similar to that shown in Fig. 1 may be obtained for materials doped with small amounts of foreign atoms. Bloem shows<sup>2</sup> that for PbS doped with  $2 \times 10^{18}$  Bi or Ag atoms per. cc. high temperature equilibrium diagrams will include regions in which the foreign atoms enter the lattice under the formation of an equal number of atomic imperfections (region of controlled vacancies) and regions in which foreign atoms are incorporated with an equal number of electronic defects (region of controlled valency). Bismuth acts as a donor in PbS, and may be written as  $\text{Bi}_{\text{Pb}}^{\cdot}$  in the Kröger-Vink notation, while silver shows acceptor behavior in lead sulfide and may be given the notation  $\text{Ag}_{\text{Pb}}^{\cdot}$ .

In addition to the above unassociated point defects, the possibility of associations between defects as a vehicle for diffusion must also be considered.

Thus we can have clustering of the form:



The law of mass action for these neutral vacancy pairs can be written as:

$$(9) \quad \frac{[v_s^{\cdot}, v_{Pb}']}{[v_s^{\cdot}] [v_{Pb}']} = K_A = K_A^0 \exp(-E_A/kt)$$

where  $E_A$  is the energy of association for the vacancy pair. The number of these  $[v_s^{\cdot}, v_{Pb}']$  complexes is independent of foreign atom concentration and sulfur pressure, and depends only on temperature. They may play an important role in diffusion of species which are prevented from moving by their normal mechanism due to the depression of the concentration of defects responsible for this mechanism.

In crystals which are doped with monovalent or trivalent cations, associations between impurities and vacancies or interstitials should also be considered in a determination of the point defects in PbS.

The concentration and type of defects predominating in a particular material constitutes but one factor which must be considered in a determination of the mechanism of diffusion. Consideration must also be given to the ratio of the diameters of the diffusing species of the compound, and to the nature of the binding forces between the components of the compound under investigation.

The ionic and covalent radii for the elements of interest in this study are given in Table 1. It is seen that if the anions are considered to diffuse as negative, divalent ions, then  $Te^{2-}$  should diffuse more slowly in PbTe than  $S^{2-}$  in PbS, since the tellurium ion is larger than the sulfur ion. Also, the size factor would indicate that  $Pb^{2+}$  should diffuse at a faster rate than any of the anions in this series of lead salts.

The processes by which diffusion occurs in the lead salts under discussion may be controlled largely by the changes in the binding forces between



components which occur on transition from the sulfide to the telluride. All these compounds are partially ionic and partially covalent, but it is difficult to make a quantitative determination of the degree to which either type exists. Scanlon<sup>9</sup> indicates that PbTe has the most homopolar character of the group while PbS, which may be 40 percent ionic, has the greatest polar character. I.M. Tsidil'kovskii<sup>10</sup> gives several examples of experimental evidence which leads to the conclusion that the covalent bond prevails in PbS.

The importance of bonding force on the predominant mode of diffusion in a material, as discussed by Arkharov and Blankova<sup>11</sup> is explained by the fact that "positively charged metalloid ions" may be obtained when the s- and p-electrons in the outer shell of the metalloid are used in forming the covalent bond. They suggest that the energy fluctuation which brings about the elementary act of diffusion causes a re-arrangement of electron density with preservation of the electro-neutrality of the aggregate of atoms which surround the metalloid ion.

It is thus seen that diffusion of metalloid ions may occur via vacancies of the metal sublattice in addition to those on the metalloid sublattice. Diffusion of the anion species in such compounds may then be enhanced as the concentration of cation vacancies increases. It is, of course, also possible for the metalloid to diffuse as a covalent species by some interstitial mechanism.

Experimentally determined diffusion coefficients will in general represent the sum of several diffusion processes which progress concurrently. If we make the assumption that the various mechanisms proceed independently and that successive movements in these mechanisms are random, we can represent the diffusion coefficient D by:

$$(10) \quad D = \sum_i \lambda_i^2 v_{i m_i}$$

where  $\lambda_1$  is the jump distance,  $\nu_1$  is the defect jump frequency, and  $m_1$  is the defect concentration for the  $i^{\text{TH}}$  diffusion mechanism.

The defect jump frequency varies with temperature according to the relation:

$$(11) \quad \nu_1 = \nu_0 \exp\left(-\frac{\Delta G_J}{RT}\right) = \nu_0 \exp\left(\frac{\Delta S_J}{R}\right) \exp\left(-\frac{\Delta H_J}{RT}\right)$$

where the pre-exponential factor,  $\nu_0$  is an atomic vibration frequency and  $\Delta G_J$ ,  $\Delta S_J$  and  $\Delta H_J$  are the Gibbs free energy, the entropy and the enthalpy per mole required to move a given defect to the top of the barrier between two equilibrium positions for a given defect.

The various defect concentrations in Eq. 10 are also found to vary exponentially with temperature so that the measured slope of a plot of  $\log D$  versus reciprocal of absolute temperature,  $1/T$ , will yield a  $\Delta H$  which is the sum of enthalpies of jumping and enthalpies of formation or association of one mole of defects.

It is seen that a study of self-diffusion as a function of sulfur pressure and foreign atom concentration over an appropriate temperature range may be useful in determination of the principal defect present in PbS. If crystals of undoped PbS are equilibrated in vessels in which the partial pressure of sulfur is high, the anion vacancy concentration should be depressed, while the concentration of sulfur interstitials might be increased, as compared with crystals heated at lower sulfur pressures. As illustrated by C. Wagner<sup>1</sup>, monovalent and trivalent cation additions may be expected to decrease and increase the cation vacancy concentration respectively in lead sulfide crystals. These effects on the defect structure of PbS must be accompanied by detectable experimentally determined diffusion coefficients of both constituents for crystals so treated.

### EXPERIMENTAL PROCEDURE

The experimental procedure followed in this study was similar to that described previously<sup>3,4</sup> in so far as synthesis of PbS, growing of single crystals and analysis of data to obtain diffusion coefficients is concerned. Lead sulfide was synthesized from the component elements, both of which were of 99.999+ percent purity.

The diffusion anneals for the PbSe study were conducted in inert atmospheres, because the pressure-temperature-composition relationships have not been ascertained for this compound. The p-T-x phase diagram of the lead-sulfur system is available<sup>9,12</sup> however. This allows for a study of diffusion as a function of stoichiometry as well as defect concentration introduced by doping, and so enables one to gain additional insight into the defect structure of lead sulfide. The details of the methods used to obtain crystals of a desired composition are found in the paper by J. Bloem<sup>2</sup>.

In the present investigation, single crystal specimens of PbS were annealed in mixtures of H<sub>2</sub>, H<sub>2</sub>S and Argon, or in closed Vycor tubes in a sulfur atmosphere. Undoped crystals were annealed in the temperature range 500-750°C so as to obtain specimens with 10<sup>18</sup> excess sulfur atoms per. cc., 10<sup>18</sup> excess lead atoms per cc. or the stoichiometric composition. At 700°C a series of crystals were annealed in partial pressures of sulfur to give concentrations varying from 5 x 10<sup>18</sup> excess lead atom per cc. to 3 x 10<sup>18</sup> excess sulfur atoms per cc. In addition, specimens doped with 0.5 mole percent Bi<sub>2</sub>S<sub>3</sub>, 0.5 mole percent Ag<sub>2</sub>S, 0.05 mole percent Bi<sub>2</sub>S<sub>3</sub> or 0.05 mole percent Ag<sub>2</sub>S were annealed under the same conditions required to obtain stoichiometric, undoped PbS. Spectrographic analysis of three undoped PbS specimens indicated that no foreign metal impurities were present in these crystals.

After the initial anneal, several drops of radioactive  $S^{35}$ , obtained from Oak Ridge National Laboratory as elemental sulfur in benzene solution, were placed on one face of single crystal specimens. The benzene was allowed to evaporate off, leaving a thin deposit of sulfur. Specimens were then annealed under identical conditions as in the original treatment, so that diffusion occurred in crystals of known stoichiometry.

Sulfur-35 emits beta radiation of maximum energy 0.167 mev, and has a half life of 87.1 days. In order to count this radiation efficiently, a flow counter was employed in conjunction with the scalar used in the previous investigations<sup>3,4</sup>. Counting was carried out on all specimens approximately three weeks from receipt of the isotope, to minimize the effects of decay with time.

Sectioning was carried out by lapping the mounted specimen over 3/0 metallographic paper under kerosene. The thickness removed was determined by taking the average of five measurements at various positions around the specimen, using a dial gage indicator calibrated in 0.0001" intervals.

Plots of activity (counts per minute) versus penetration in  $cm^2$  are shown in Figs. 2 and 3. Values of  $D$  calculated from the slopes of the activity-penetration plots are included in Table II. Although the sides of each specimen were carefully ground to eliminate effects of surface diffusion, it is believed that phenomena of this kind are responsible for the tails observed on some of the activity-penetration curves.

#### RESULTS AND DISCUSSION

In Fig. 4 are included least squares plots of  $\log_{10} D$  versus reciprocal of absolute temperature for specimens of undoped PbS which were prepared under conditions described above. Figures 5 and 6 show analogous plots obtained for the diffusion of  $S^{35}$  in PbS doped with  $Bi_2S_3$  and  $Ag_2S$  respectively. The curves

presented in Figs. 4 to 6 can be described by Arrhenius type equations of the form:

$$(12) D = D_0 \exp(-E/kt)$$

where  $T$  is the absolute temperature,  $D_0$  is the frequency factor in  $\text{cm}^2/\text{sec}$ ,  $E$  is the experimental activation energy in electron volts, and  $k$  is Boltzmann's constant. The values obtained for  $D_0$  and  $E$  are presented in Table III, together with similar data for  $\text{Pb}^{210}$  in stoichiometric  $\text{PbS}^4$ ,  $\text{Pb}^{210}$  in  $\text{PbSe}$  containing  $10^{18}$  holes per  $\text{cc}^3$ ,  $\text{Se}^{75}$  in  $\text{PbSe}$  containing less than  $10^{18}$  electrons per  $\text{cc}^{13}$  and  $\text{Te}^{127}$  in  $\text{PbTe}$  containing  $10^{17}$  holes per  $\text{cc}^{13}$ . There is presently no data available for the self diffusion of a lead tracer in  $\text{PbTe}$ .

Several conclusions may be drawn from a study of these experimental results. First, evidence that sulfur does not diffuse predominantly by a simple anion vacancy mechanism is obtained directly from the data presented in Figs. 4 and 5. It is seen from Fig. 4 that sulfur diffuses at a faster rate in crystals which have been equilibrated so as to produce an excess of sulfur, as compared with diffusivities found for crystals containing an excess of lead. If sulfur were to diffuse by jumping into vacancies in the sulfur sublattice then diffusion of sulfur would be enhanced in lead excess crystals (containing relatively more anion vacancies), and diminished in sulfur excess crystals, where the concentration of anion vacancies is greatly depressed. The high activation energy found for diffusion of sulfur in stoichiometric  $\text{PbS}$  is probably related to the small defect concentration existing in this material, as compared with non-stoichiometric and doped crystals.

The data obtained from doped  $\text{PbS}$  crystals must also be considered in an attempt to determine the mechanism of diffusion of sulfur. Diffusion coefficients of  $\text{S}^{35}$  in  $\text{PbS}$  doped with  $\text{Bi}_2\text{S}_3$  are found to increase with increasing impurity concentration, with an attending decrease in experimental activation

energy as higher impurity levels are approached. See Fig. 5. If  $\text{Bi}_2\text{S}_3$  enters the lead sulfide lattice under the formation of cation vacancies as stated by C. Wagner<sup>1</sup>, the case against a simple anion vacancy mechanism is strengthened by this information, since the anion vacancy concentration should be extremely small in these crystals heavily doped with  $\text{Bi}_2\text{S}_3$ . The experimental results indicate that diffusion of sulfur in PbS is increased with increasing cation vacancy concentration.

The results obtained for crystals doped with  $\text{Ag}_2\text{S}$  (see Fig. 6) cannot be easily interpreted because the limit of solid solubility may have been exceeded here. Whereas PbS can dissolve 3 to 5 percent of  $\text{Bi}_2\text{S}_3$ <sup>14</sup> at the temperatures of interest in this paper, the solubility of  $\text{Ag}_2\text{S}$  in PbS is of the order of 0.1 to 0.4 percent<sup>14</sup> in the same temperature range. This may explain the almost identical diffusion characteristics found for  $\text{S}^{35}$  in PbS crystals which were doped with 0.5 and 0.05 mole percent  $\text{Ag}_2\text{S}$ . If the solubility of  $\text{Ag}_2\text{S}$  in PbS is sufficiently small, it is possible that the monovalent cation enters the lead sulfide crystal under the formation of electronic defects at the sulfur partial pressures employed in this study, and that the atomic defect concentrations are relatively similar for undoped PbS and for lead sulfide doped with  $\text{Ag}_2\text{S}$ .

It is seen from Figs. 5 and 6 that low diffusivities were found at 500°C for PbS doped with  $\text{Bi}_2\text{S}_3$  or  $\text{Ag}_2\text{S}$ . It is believed that these depressed diffusion coefficients result from the association of the foreign atoms with native atomic imperfections. Measurements of dielectric loss on several other systems indicate that such association occurs in all cases at low temperatures<sup>7</sup>. Further work is necessary in the temperature region indicated by dotted lines in Figs. 5 and 6, before definite statements can be made concerning the low diffusivities found for doped specimens.

From the data presented thus far, it is possible to conclude that sulfur does not diffuse through PbS by a simple anion vacancy mechanism. Several alternatives are possible. Among these are (1) diffusion by some interstitial mechanism, (2) diffusion of sulfur as neutral, or positively charged species through vacancies in the cation sublattice, and (3) diffusion via vacancy pairs. We now consider these.

One can postulate that sulfur diffuses as a divalent negative anion via an interstitial mechanism. It appears however that the  $S^{2-}$  ion, with a radius of  $1.84 \text{ \AA}$ , is far too large to be a mobile interstitial species, if PbS is considered to be built up of  $S^{2-}$  ions, and  $Pb^{2+}$  ions of radius  $1.32 \text{ \AA}$ . Thus, diffusion of  $S^{2-}$  by an interstitial mechanism is eliminated as the mode for transport of sulfur through lead sulfide. This is not to say that sulfur does not diffuse by an interstitial mechanism in some form other than as a divalent negative ion.

There is evidence which indicates that the metalloids do not under normal circumstances diffuse in the lead salts as divalent negatively charged anions. If they did, then the variation in size of the ions would lead one to believe that  $S^{2-}$  should be the most mobile species of the three, with  $Se^{2-}$  intermediate and  $Te^{2-}$ , the largest and slowest diffusing of the metalloids in the lead salts. As can be seen from Fig. 7, in which have been plotted values of  $\log_{10} D$  versus  $1/T$  for diffusion of the metalloids in PbS, PbSe and PbTe, just the opposite is found experimentally. Tellurium diffuses at a rate almost three orders of magnitude faster than sulfur at the temperatures of interest. Higher self-diffusion coefficients are found for the tellurium than for sulfur, even after normalizing the temperatures of diffusion to the same fraction of the melting temperature for PbS and PbTe. In addition, the activation energy for  $Te^{127}$  in PbTe is shown in Table III to be 0.75ev, whereas that for diffusion of  $S^{35}$  in

stoichiometric PbS is found to be considerably higher, 1.38ev. These results are in agreement with those of Arkharov and Blankova<sup>11</sup> for the transition metal chalcogenides of Ti, V and Co, where marker experiments show tellurium to be most mobile and sulfur the least mobile for a given family of compounds.

Further information regarding the form in which sulfur is transported through PbS is obtained from comparison of the diffusion characteristics of lead and sulfur in stoichiometric PbS. The similar activation energies, and higher diffusivities found for S<sup>35</sup> as compared with those for Pb<sup>210</sup> are in contrast to the values one would expect if lead and sulfur diffused as divalent positive and negative ions respectively. In that case, the data of Table I suggests an anion/cation diameter ratio of 1.4 which would indicate a far greater mobility for the cation species as compared with the anion. The results of this study, which shows that sulfur diffuses at a faster rate than lead in lead sulfide, are in agreement with the marker experiments of Dorin and Filaretova<sup>15</sup>. In that work, a hole was made in a layer of lead sulfide which had been formed when a lead specimen was placed in molten sulfur. The specimen was again immersed in the sulfur bath for several hours. Upon removal, it was found that the distance from the hole to the boundary adjacent to the lead had changed considerably while that to the sulfur boundary had remained unchanged. This indicates that the PbS layer grows by the penetration of sulfur through the layer, to the metal substrate.

It appears that sulfur does not diffuse through PbS as S<sup>2-</sup> via a simple anion vacancy or interstitial type mechanism. The possibility remains that S<sup>2-</sup> ions may diffuse by a more complex mechanism. One such mode which is given serious consideration in discussions of anion diffusion in classical ionic materials<sup>16,17</sup> is that in which neutral vacancy pairs are claimed to be the vehicle for the motion of negatively charged anions. As has been pointed out



earlier in this paper, the number of neutral pairs is a function solely of temperature, and should be independent of composition. It has been shown that the diffusion rate of sulfur in PbS is dependent on crystal composition (see Fig. 4), thus ruling out diffusion via vacancy pairs as the predominant mechanism.

In Fig. 8 we have plotted the results of an experiment to determine the composition dependence of  $S^{35}$  diffusion at  $700^{\circ}\text{C}$ . Each circle in this figure represents the average of several experimental values obtained for a given sulfur pressure. Two straight lines can be drawn through the experimental points, with the break occurring at the sulfur pressure corresponding to stoichiometric PbS. On the excess sulfur side  $D_s^{35}$  is found to be proportional to  $p_{s_2}^{0.383}$  while on the lead excess side of stoichiometry  $D_s^{35}$  varies as  $p_{s_2}^{0.200}$ . In addition we have plotted an experimental point shown at the lower right of Fig. 8 which indicates an increase in the diffusion rate of  $S^{35}$  at sulfur pressures corresponding to lead sulfide with approximately  $5 \times 10^{18}$  excess lead atoms per cc. This is a good indication that several mechanisms may be operative simultaneously, with the different straight line portions of Fig. 8 representing different ranges in the  $\ln$  concentration versus  $\ln p_{s_2}^{1/2}$  diagram shown in Fig. 1. Although the slopes of the experimental lines shown in Fig. 8 do not fit those shown in the theoretical diagram of Fig. 1 it is nevertheless worthwhile to note that the two linear regions in which  $D_s^{35}$  decreases with decreasing sulfur pressure, followed by a region in which  $D_s^{35}$  increases with further decreasing sulfur pressure are predicted theoretically in Fig. 1. However the experimental results can be explained on the basis of the diffusion of  $S^{35}$  through either an interstitial mechanism or by some cation vacancy mechanism. The latter can occur only if sulfur diffuses as a positive or neutral species.

Possible modes of diffusion of sulfur in lead sulfide in which the diffusing species is the  $S^{2-}$  ion seem to be ruled out by experimental results. It remains to consider processes by which sulfur may diffuse in some other form. As was mentioned previously, a better understanding of the mechanism of diffusion may be obtained from an analysis of the binding forces between the components of the lead sulfide lattice. For the case of PbS the nature of the interatomic forces is such that both ionic and covalent type bonds are present. It has been stated that evidence exists which supports the hypothesis that covalent binding represents the major cohesive force in PbS. It is conceivable that the presence of covalent bonding forces between lead and sulfur creates a situation in which the sulfur may diffuse through PbS as a small positively charged atom rather than as a large negatively charged atom. In this situation diffusion could take place by sulfur jumps into cation vacancy sites or through an interstitial mechanism.

The exact process by which electron exchange occurs in PbS is not known. Coulson<sup>18</sup> points out that tetrahedral bonds found in ZnS arise partly from atomic  $Zn^=$  and  $S^{++}$ , both of which then adopt  $sp^3$  hybridization. The tetrahedral bonds found in ZnS can be explained in this manner.

In the case described by Arkharov and Blankova<sup>11</sup>, electron exchange occurs between metalloid and metal atoms of the transition metal chalcogenides by a sharing of p- and s- electrons of the metalloid with d- electrons of the metal.

Lead sulfide crystallizes in the Na Cl, cubic structure however, so an explanation of the formation of covalent bonds in this material must include a method by which such bonds form at right angles. If it is assumed that the covalent bonds arise from atomic  $Pb^-$  and  $S^+$ , as the result of local rearrangement of electron density, then it is found that the outer shells for  $Pb^-$  are given by  $6s^2 6p^3$  while those for  $S^+$  are  $3s^2 3p^3$ . We thus have a

situation in which the outer p- orbitals of each component of PbS have three electrons available for forming covalent bonds. Since p- orbitals are at right angles it is possible for covalent bonds to exist within the Na Cl structure found for lead sulfide.

A self consistant explanation of much of the experimental results cited in this paper is possible if one accepts the theory that local rearrangements of electron density can bring about the formation of small positively charged metalloid atoms in PbS, PbSe and PbTe.

The idea that sulfur can diffuse not only through vacancies in its own sublattice, but through cation vacancies, now becomes reasonable, and must be considered when interpreting the results presented in Figure 4, which indicate that sulfur diffuses most rapidly in crystals containing sulfur concentrations in excess of the stoichiometric ratio. The argument for a cation vacancy mechanism is strengthened by the high diffusivities and low activation energy found for crystals which were doped with  $\text{Bi}_2\text{S}_3$ . While  $\text{Bi}_2\text{S}_3$  might enter lead sulfide under the formation of interstitial sulfur atoms rather than cation vacancies, the low activation energies found for specimens doped with  $\text{Bi}_2\text{S}_3$ , as compared with the value determined from undoped, stoichiometric PbS, is taken as evidence that cation vacancies are indeed the defect formed by the impurity addition. The possibility that sulfur diffuses by an interstitial mechanism cannot be ruled out, but experimental evidence favors the cation vacancy mechanism.

The increase in diffusion rate found for crystals annealed in the lowest sulfur partial pressure is taken to mean that the cation vacancy concentration has been depressed to the point where diffusion of sulfur ions through anion vacancies becomes the predominant mode of diffusion.

Next we consider the experimental values found for the pre-exponential factors as given in Table III. It should be noted that the values listed for this factor are all several orders of magnitude lower than are generally quoted when diffusion occurs by a process of single atomic jumps, as in the case of the f.c.c. metals and the alkali halides. Pound et.al.<sup>19</sup> have pointed out however, in their analysis of diffusion in the b.c.c. metals that a low Arrhenius factor may be an indication of a thermally activated process which requires the simultaneous movement of several atoms. Thus there is one more indication that the mechanism of diffusion of sulfur in PbS does not involve the simple migration via single atomic jumps, but rather a process in which several atoms may participate.

#### CONCLUSIONS

1. The nature of the bonding forces between the components of a system may be the most important single factor in determining the process by which diffusion occurs in partially polar compounds.
2. For the compound lead sulfide, it is suggested that sulfur normally diffuses as a small, positively charged atom surrounded by metal ions with locally varied valence, a condition brought about by the local redistribution of electron density required to form covalent bonds.
3. It is believed that diffusion of the anion species in lead sulfide occurs predominantly by the movement of small, positively charged sulfur atoms, either through jumps onto vacancies in the cation sublattice, or by some interstitial mechanism.
4. For crystals of lead sulfide containing large excess of lead, sulfur may diffuse through vacancies in the sulfur sublattice, as a divalent negative ion.

5. The increase in mobility found for the metalloid atoms on going from the lead salts of sulfur, to the selenide and telluride is attributed to the greater degree of covalent bonding associated with the salts having metalloid component with high atomic number.

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Table I

Atomic and Ionic Radii of Elements

<u>ELEMENT</u>	<u>-2</u>	<u>+2</u>	<u>COVALENT</u>
Sulfur	1.84		1.04
Selenium	1.98		1.17
Tellurium	2.21		1.37
Lead		1.32	

Table II

Specimen	Approximate Composition	$\log P_{S_2}$ (atm)	Temp ( $^{\circ}\text{C}$ )	Time (sec)	$D$ ( $\text{cm}^2/\text{sec}$ )
S-29	Stoich. PbS	-5.00	500	$1.602 \times 10^6$	$8.47 \times 10^{-14}$
S-30		-5.00	500	$1.602 \times 10^6$	$6.09 \times 10^{-14}$
S-1		-3.62	600	$5.85 \times 10^5$	$7.56 \times 10^{-13}$
S-2		-3.62	600	$5.85 \times 10^5$	$6.14 \times 10^{-13}$
S-18		-2.75	700	$2.088 \times 10^5$	$3.71 \times 10^{-12}$
S-79		-2.31	750	$1.656 \times 10^5$	$1.43 \times 10^{-11}$
S-80		-2.31	750	$1.656 \times 10^5$	$1.04 \times 10^{-11}$
S-21	$\text{PbS} + 10^{18}$ S per cc.	-0.00	500	$1.602 \times 10^6$	$4.47 \times 10^{-13}$
S-22		-0.00	500	$1.602 \times 10^6$	$5.17 \times 10^{-13}$
S-6		-0.25	600	$5.922 \times 10^5$	$4.02 \times 10^{-12}$
S-67		-0.75	650	$4.824 \times 10^5$	$5.79 \times 10^{-12}$
S-68		-0.75	650	$4.824 \times 10^5$	$8.28 \times 10^{-12}$
S-13		-1.00	700	$2.088 \times 10^5$	$2.39 \times 10^{-11}$
S-14		-1.00	700	$2.088 \times 10^5$	$3.36 \times 10^{-11}$
S-45		-1.25	750	$1.728 \times 10^5$	$2.91 \times 10^{-11}$
S-46		-1.25	750	$1.728 \times 10^5$	$4.97 \times 10^{-11}$
S-26	$\text{PbS} + 10^{18}$ Pb per cc.	-8.00	500	$1.602 \times 10^6$	$5.26 \times 10^{-14}$
S-9		-6.75	600	$5.688 \times 10^5$	$3.46 \times 10^{-13}$
S-10		-6.75	600	$5.688 \times 10^5$	$3.43 \times 10^{-13}$
S-63		-5.50	650	$4.212 \times 10^5$	$6.07 \times 10^{-13}$
S-64		-5.50	650	$4.212 \times 10^5$	$1.44 \times 10^{-12}$
S-71		-4.62	700	$2.736 \times 10^5$	$3.30 \times 10^{-12}$
S-72		-4.62	700	$2.736 \times 10^5$	$1.77 \times 10^{-12}$
S-53		-3.625	750	$1.836 \times 10^5$	$4.36 \times 10^{-12}$



Table II - (continued)

Specimen	Approximate Composition	$\log P_{S_2}$ (atm)	Temp ( $^{\circ}\text{C}$ )	Time (sec)	$D$ ( $\text{cm}^2/\text{sec}$ )
S-88	PbS + $3 \times 10^{18}$ S per cc.	0.00	700	$3.32 \times 10^5$	$4.18 \times 10^{-11}$
S-87	PbS + $3 \times 10^{18}$ S per cc.	0.00	700	$3.32 \times 10^5$	$6.46 \times 10^{-11}$
S-89	PbS + $5 \times 10^{17}$ S per cc.	-2.00	700	$2.556 \times 10^5$	$8.96 \times 10^{-12}$
S-90	PbS + $5 \times 10^{17}$ S per cc.	-2.00	700	$2.556 \times 10^5$	$8.85 \times 10^{-12}$
S-83	PbS + $3 \times 10^{18}$ Pb per cc.	-5.75	700	$2.736 \times 10^5$	$1.28 \times 10^{-12}$
S-84	PbS + $3 \times 10^{18}$ Pb per cc.	-5.75	700	$2.736 \times 10^5$	$1.12 \times 10^{-12}$
S-85	PbS + $5 \times 10^{18}$ Pb per cc.	-7.00	700	$2.574 \times 10^5$	$1.87 \times 10^{-12}$
S-86A	PbS + $5 \times 10^{18}$ Pb per cc.	-7.00	700	$2.574 \times 10^5$	$1.67 \times 10^{-12}$
Bi-19	PbS + $\frac{1}{2}$ mole % $\text{Bi}_2\text{S}_3$ ↓	-5.00	500	$1.699 \times 10^5$	$9.22 \times 10^{-14}$
Bi-20		-5.00	500	$1.699 \times 10^5$	$9.95 \times 10^{-14}$
Bi-1		-3.62	600	$5.85 \times 10^5$	$5.15 \times 10^{-12}$
Bi-2		-3.62	600	$5.85 \times 10^5$	$3.43 \times 10^{-12}$
Bi-16		-3.125	650	$4.212 \times 10^5$	$6.88 \times 10^{-12}$
Bi-5		-2.75	700	$2.088 \times 10^5$	$1.11 \times 10^{-11}$
Bi-6		-2.75	700	$2.088 \times 10^5$	$6.56 \times 10^{-12}$
Bi-9		-2.31	750	$1.692 \times 10^5$	$1.86 \times 10^{-11}$
Bi-11		-2.31	750	$1.656 \times 10^5$	$1.10 \times 10^{-11}$
Bi-12		-2.31	750	$1.656 \times 10^5$	$2.32 \times 10^{-11}$
B-19	PbS + $\frac{1}{20}$ mole % $\text{Bi}_2\text{S}_3$ ↓	-5.00	500	$1.699 \times 10^6$	$3.58 \times 10^{-14}$
B-20		-5.00	500	$1.699 \times 10^6$	$4.39 \times 10^{-14}$
B-1		-3.62	600	$5.85 \times 10^5$	$1.48 \times 10^{-12}$
B-2		-3.62	600	$5.85 \times 10^5$	$1.26 \times 10^{-12}$
B-15		-3.125	650	$5.076 \times 10^5$	$4.98 \times 10^{-12}$

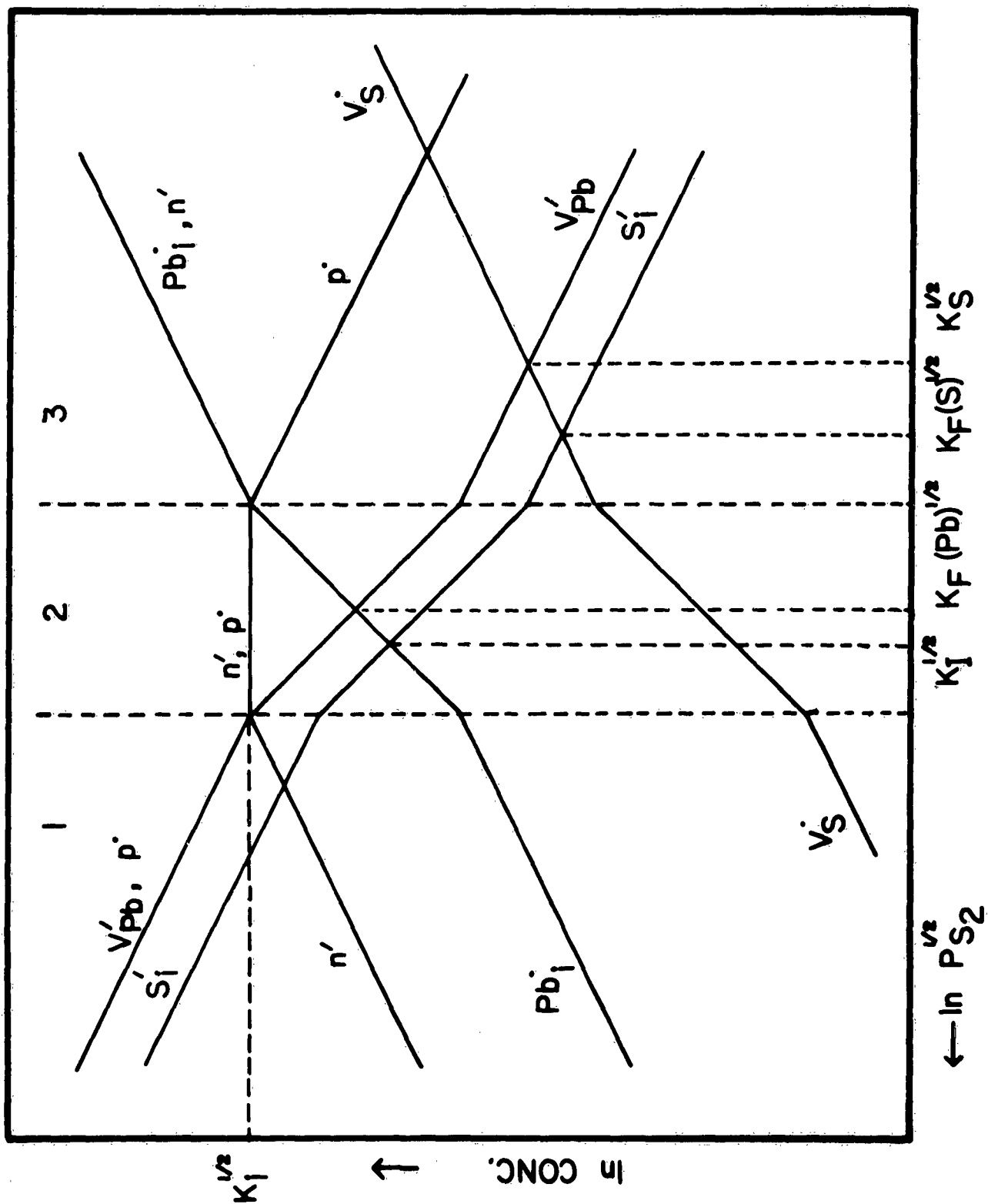
Table II - (continued)

Specimen	Approximate Composition	$\log P_{S_2}$ (atm)	Temp ( $^{\circ}\text{C}$ )	Time (sec)	$D$ ( $\text{cm}^2/\text{sec}$ )
B-16	$\text{PbS} + \frac{1}{20} \text{ mole } \% \text{ Bi}_2\text{S}_3$	-3.125	650	$5.076 \times 10^5$	$4.63 \times 10^{-12}$
B-5	↓	-2.75	700	$2.088 \times 10^5$	$2.60 \times 10^{-12}$
B-6		-2.75	700	$2.088 \times 10^5$	$3.04 \times 10^{-12}$
B-21		-2.31	750	$1.656 \times 10^5$	$8.51 \times 10^{-12}$
B-22		-2.31	750	$1.656 \times 10^5$	$1.82 \times 10^{-11}$
Ag-21	$\text{PbS} + \frac{1}{2} \text{ mole } \% \text{ Ag}_2\text{S}$	-5.00	500	$1.699 \times 10^6$	$6.64 \times 10^{-14}$
Ag-22	↓	-5.00	500	$1.699 \times 10^6$	$7.51 \times 10^{-14}$
Ag-17		-3.62	600	$5.688 \times 10^5$	$1.18 \times 10^{-12}$
Ag-18		-3.62	600	$5.688 \times 10^5$	$1.14 \times 10^{-12}$
Ag-14		-3.125	650	$4.212 \times 10^5$	$3.88 \times 10^{-12}$
Ag-1		-2.75	700	$2.628 \times 10^5$	$6.26 \times 10^{-12}$
Ag-2		-2.75	700	$2.628 \times 10^5$	$5.29 \times 10^{-12}$
Ag-7		-2.31	750	$1.692 \times 10^5$	$1.46 \times 10^{-11}$
A-21	$\text{PbS} + \frac{1}{20} \text{ mole } \% \text{ Ag}_2\text{S}$	-5.00	500	$1.699 \times 10^6$	$1.80 \times 10^{-13}$
A-17	↓	-3.62	600	$5.688 \times 10^5$	$1.25 \times 10^{-12}$
A-18		-3.62	600	$5.688 \times 10^5$	$1.14 \times 10^{-12}$
A-13		-3.125	650	$5.076 \times 10^5$	$4.67 \times 10^{-12}$
A-23		-3.125	650	$5.616 \times 10^5$	$3.97 \times 10^{-12}$
A-2		-2.75	700	$2.628 \times 10^5$	$6.90 \times 10^{-12}$
A-7		-2.31	750	$1.692 \times 10^5$	$1.23 \times 10^{-11}$
A-8		-2.31	750	$1.692 \times 10^5$	$1.37 \times 10^{-11}$
A-9		-2.31	750	$1.656 \times 10^5$	$9.12 \times 10^{-12}$

Table III

<u>Composition</u>	<u>Diffusing Species</u>	<u><math>\epsilon</math> (ev)</u>	<u><math>D_0</math> (<math>\frac{\text{cm}^2}{\text{sec}}</math>)</u>
Stoichiometric PbS	$\text{S}^{35}$	1.38	$3.80 \times 10^{-5}$
PbS + $10^{18}$ excess S per cc.	$\text{S}^{35}$	1.22	$4.56 \times 10^{-5}$
PbS + $10^{18}$ excess Pb per cc.	$\text{S}^{35}$	1.16	$1.89 \times 10^{-6}$
PbS + $1/2$ mole % $\text{Ag}_2\text{S}$	$\text{S}^{35}$	1.26	$2.39 \times 10^{-4}$
PbS + $1/20$ mole % $\text{Ag}_2\text{S}$	$\text{S}^{35}$	1.12	$4.11 \times 10^{-5}$
PbS + $1/2$ mole % $\text{Bi}_2\text{S}_3$	$\text{S}^{35}$	0.69	$3.82 \times 10^{-7}$
PbS + $1/20$ mole % $\text{Bi}_2\text{S}_3$	$\text{S}^{35}$	0.93	$3.38 \times 10^{-6}$
Stoichiometric $\text{PbS}^3$	$\text{Pb}^{210}$	1.38	$2.31 \times 10^{-4}$
PbSe with $10^{18}$ holes/cc. <sup>2</sup>	$\text{Pb}^{210}$	0.83	$4.98 \times 10^{-6}$
PbSe <sup>11</sup>	$\text{Se}^{75}$	1.2	$2.1 \times 10^{-5}$
PbTe with $10^{17}$ holes/cc. <sup>11</sup>	$\text{Te}^{127}$	0.75	$2.7 \times 10^{-6}$

Fig. 1. High temperature equilibrium for undoped PbS.



Figs. 2 and 3. Typical penetration curves in PbS.

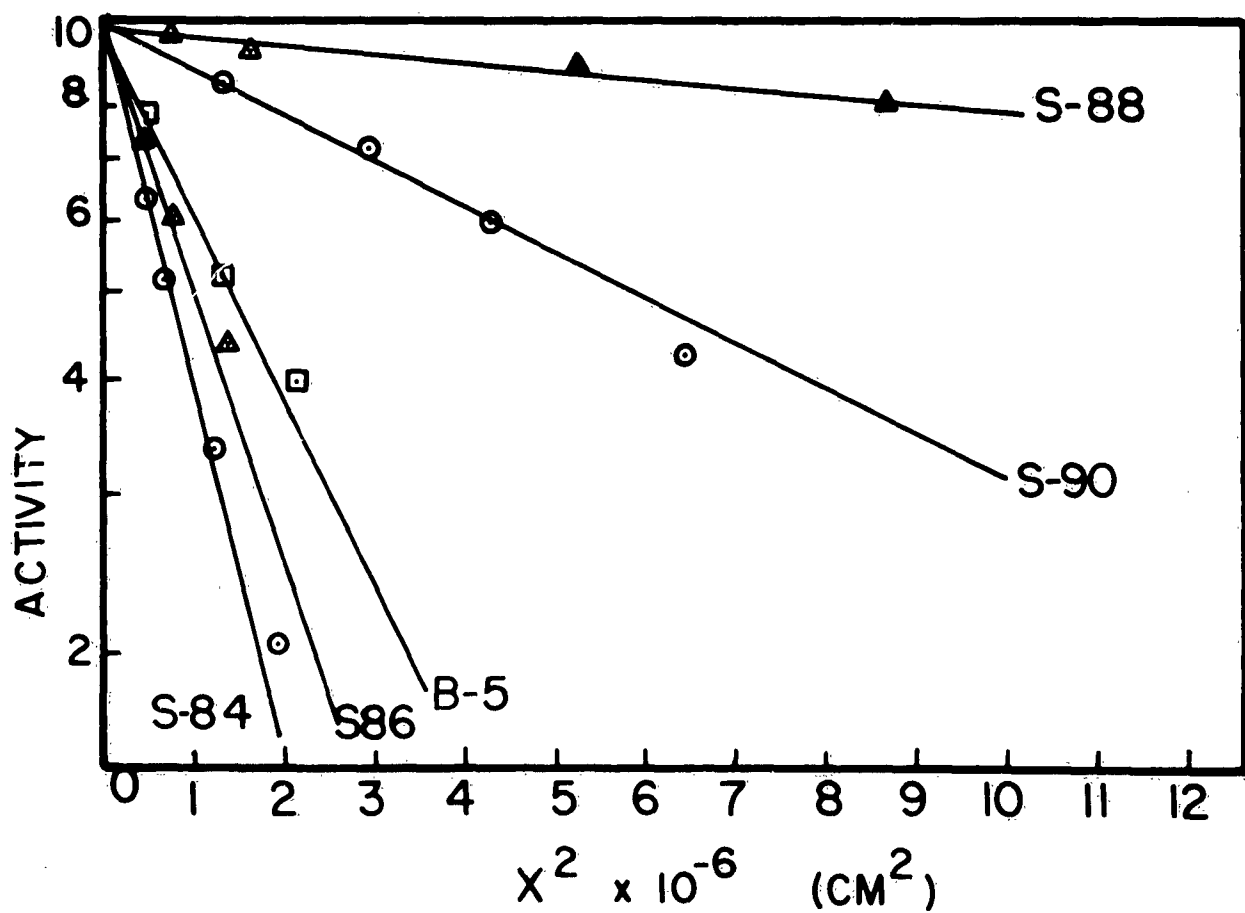
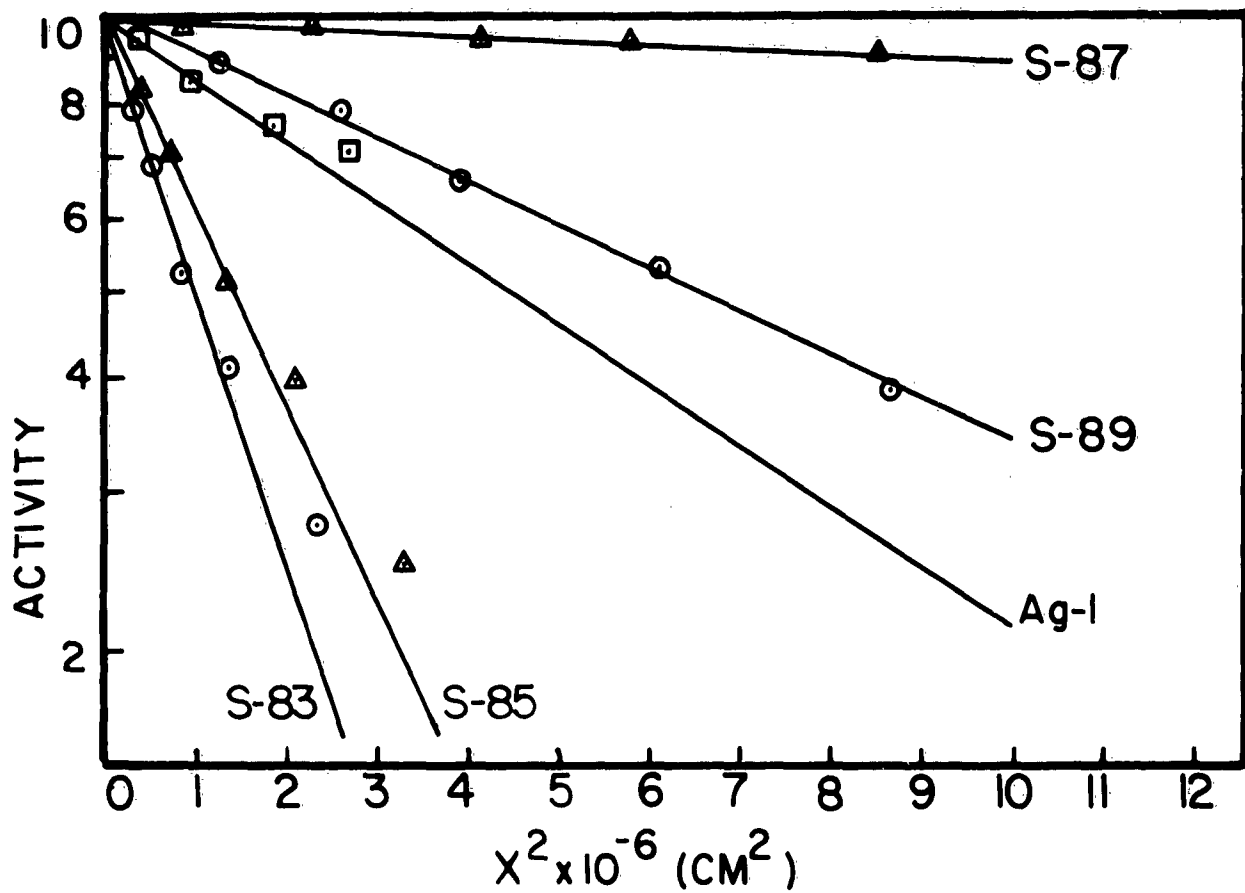


Fig. 4. Temperature variation of the diffusion coefficients for  $S^{35}$  in PbS.



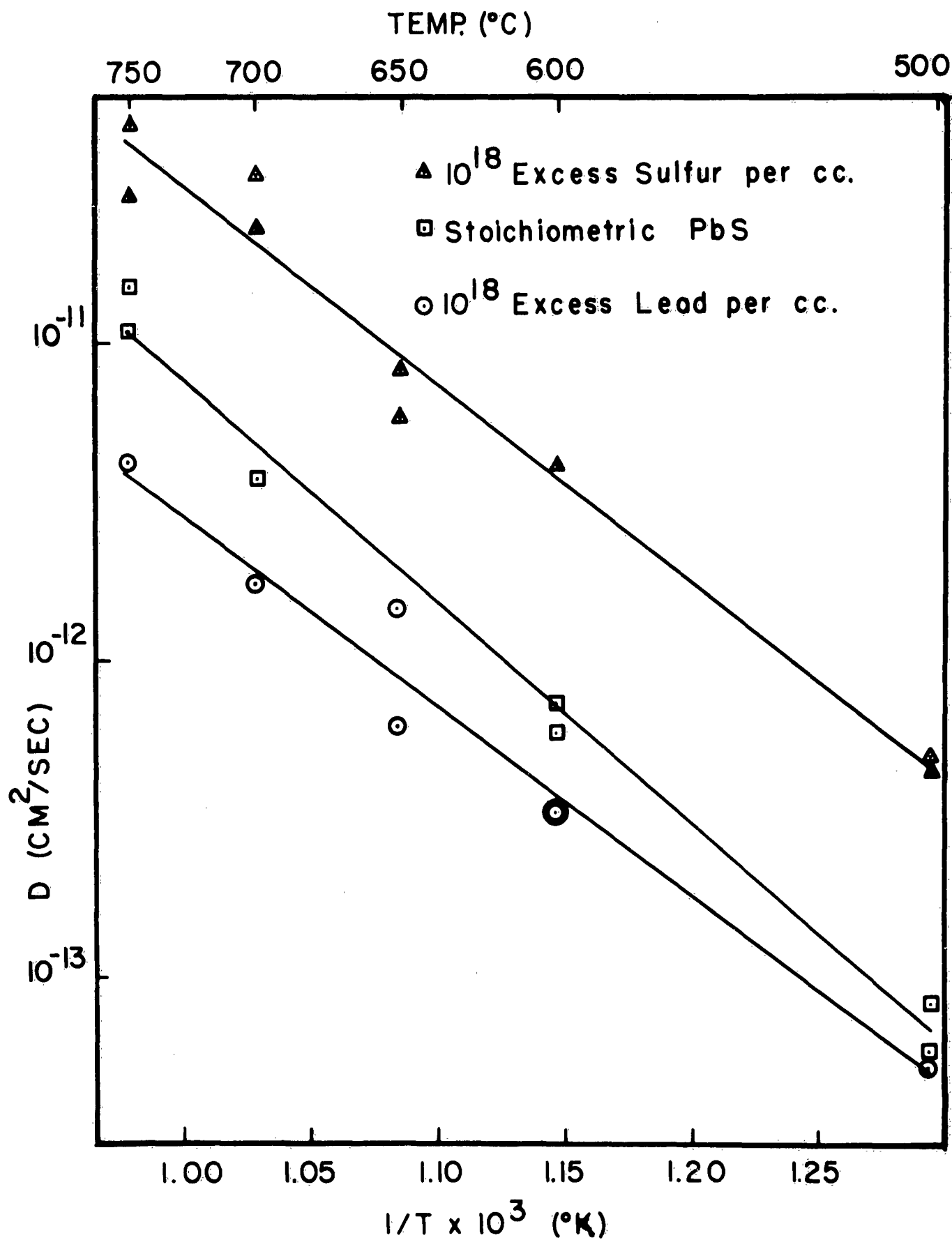


Fig. 5. Temperature variation of the diffusion coefficients for  $S^{35}$  doped  
with  $Bi_2S_3$ .

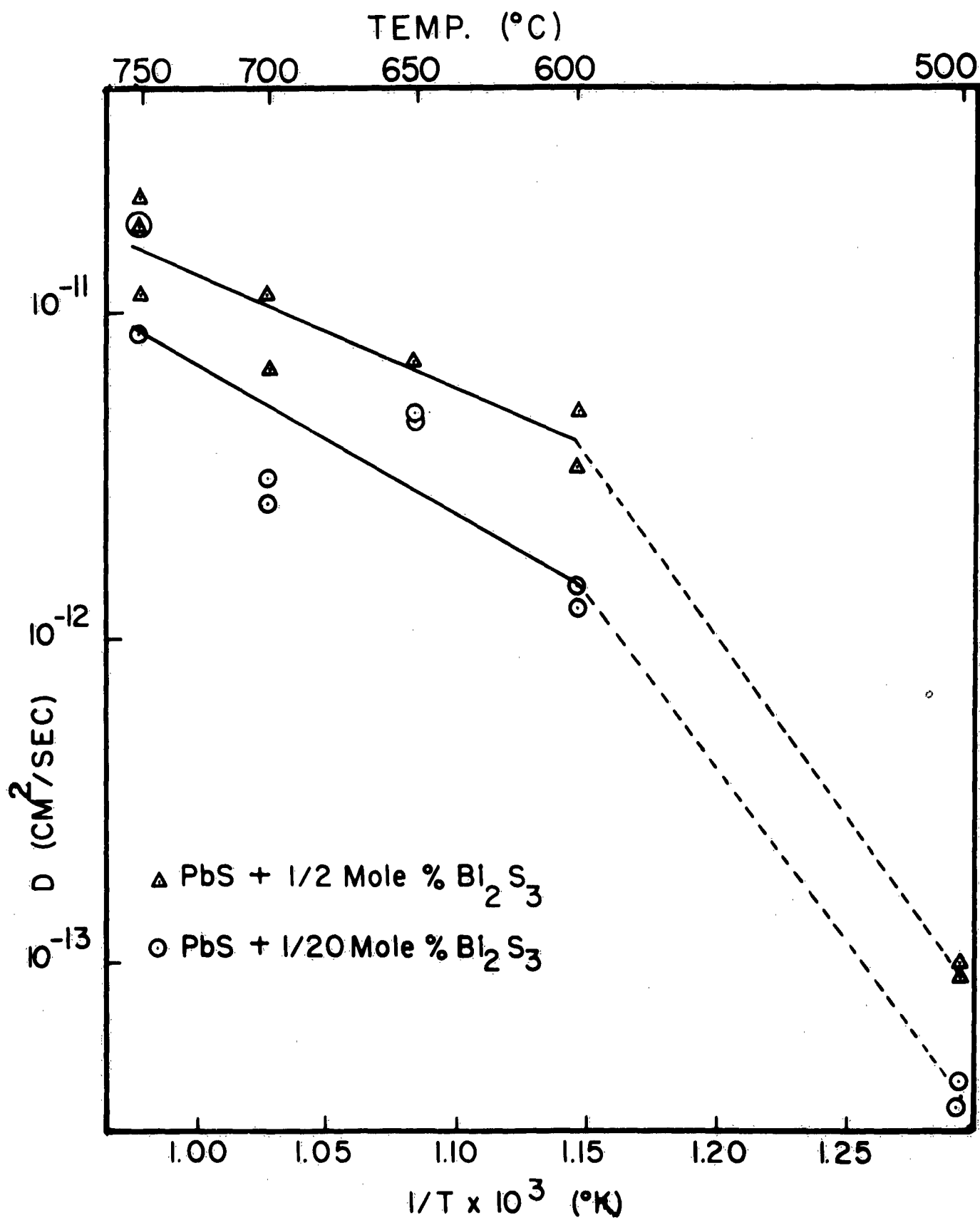


Fig. 6. Temperature variation of the diffusion coefficients for  $S^{35}$  in PbS doped with  $Ag_2S$ .

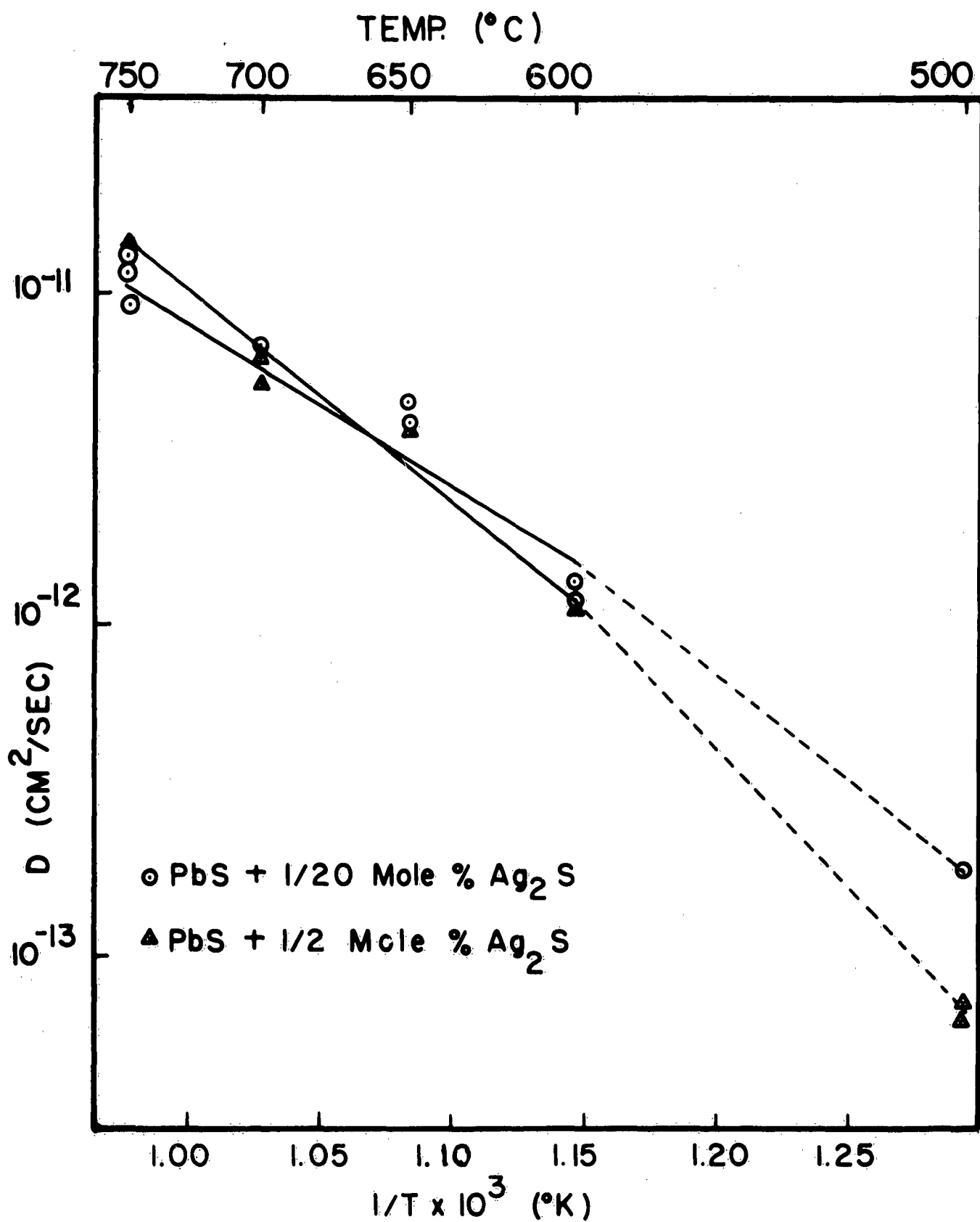


Fig. 7. Temperature variation of the diffusion coefficients for  $S^{35}$  in PbS,  $Se^{75}$  in PbSe, and  $Te^{127}$  in PbTe.

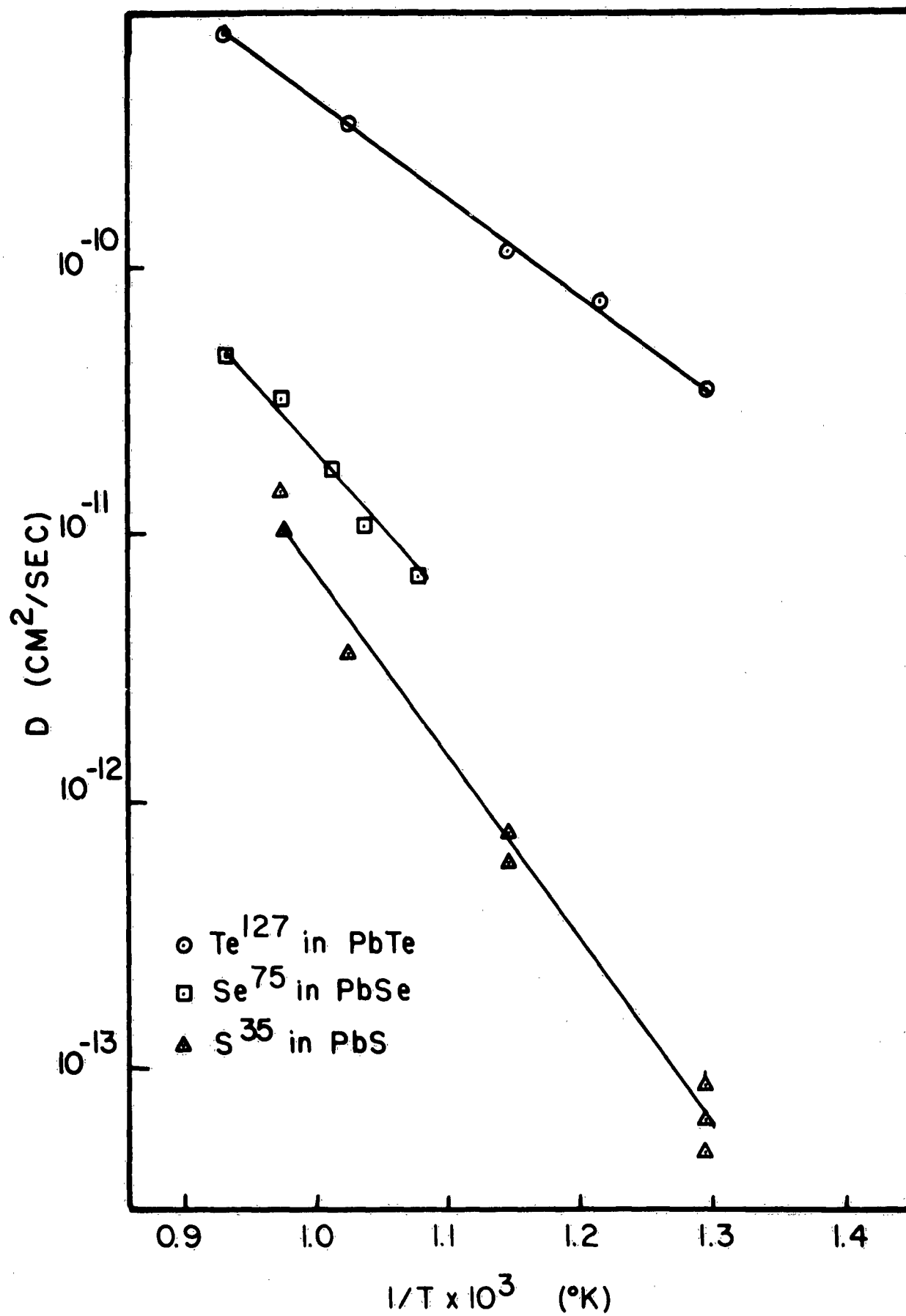


Fig. 8. Pressure variation of the diffusion coefficients for  $S^{35}$  in PbS.



